

TITLE OF INVENTION

EXTENDED RETENTION AND MEDIUM CONSISTENCY PULP TREATMENT

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] Not Applicable

5 STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not Applicable

BACKGROUND OF THE INVENTION

[0003] This invention relates to the processing of cellulosic fibrous material in preparation for use in papermaking. In particular, the invention is directed to a
10 process for enhancing the delignification of cellulosic fibrous material preparatory to (especially ECF) bleaching of the pulp.

[0004] In the papermaking industry it is common practice to digest chips or like particulates of a cellulosic fibrous material, such as wood chips, with a view to separating the cellulosic fibers from the lignin which binds the fibers to one another
15 and to produce a pulp. This process step is commonly termed "digestion" and is a major step in "delignification" of the pulp. Various chemicals and various process steps are employed in the digestion of different types of chips. Particularly, softwood and hardwood chips are employed as starting materials in a papermaking process. Lignin is responsible for the brown coloration of paper. Kappa number is an index
20 used by the pulp and paper industry to express the lignin content of a pulp. Many mills employ oxygen (O₂) for further delignification of pulp before ECF bleaching. Excessive removal of lignin (delignification) in digestion and/or O₂ delignification operations tend to degrade the mechanical strength of the cellulosic fibers.

[0005] The output from a digester contains the liquor employed in the digestion
25 process, individual separated fibers, clumps of fibers, those materials which are the

byproducts of the digestion of the lignin such as resins, phenolics, nonphenolics, hexenuronic acid ("Hex-A"), trash, and other matter (collectively, "brown stock").

[0006] Depending upon the intended end use of the paper to be made from the pulp, the brown stock may be washed, and/or O₂ delignified (for some mills) followed by bleaching to enhance various of its properties, such as brightness, dirt removal, etc. Bleaching commonly is carried out in stages, each stage being designed to effect one or more desirable enhancements of the pulp. Three to five stages are common in a bleach plant. The first two stages (D₀E_{OP}) of current employed in bleach plants are also delignification stages. As is recognized in the art, each stage comprises a reaction tower and each tower is preceded by a washer. In the present instance, when identifying stages of a bleach plant washers are at times, merely assumed.

[0007] In typical multi-stage elemental chlorine free (ECF) bleach plants, the first chlorine dioxide stage (D₀) is for delignification and the other following stages (D₁ and D₂ for example) are for bleaching (brightness development, dirt removal for pulp cleanness. Pulp (fiber) strength is a factor in all stages. Because of this difference in objectives of these stages, the D₀ stage of a typical current bleach plant is operated at significantly different operating parameters from the operating parameters of the remaining following stages. Pertinent ones of these operational parameters for currently existing bleach plants as given in Table I below:

TABLE I

	D ₀	D ₁ or D ₂
Consistency, %	3-4	10-12
Retention time, min.	25-45 (<60)	120-180
Steam consumption	no	yes
Temperature, °C	50-65	65-80
pH	2-3	3-4

[0008] In past years, the first stage, D₀, of a bleach plant used elemental chlorine at low pulp consistency and short retention time within a reaction vessel (tower) for delignification because of high reactivity of elemental chlorine toward both phenolic and nonphenolic lignin. In converting the traditional elemental chlorine-based bleach plants to elemental chlorine-free (ECF) bleach plants to, among other things, eliminate the formation of dioxins produced in elemental chlorine-based pulp bleaching operations, a majority of the existing mills simply converted the old chlorine (C or C₁) stage to a chlorine dioxide (D₀) stage, using the existing tower equipment. This practice is largely based on the conventional wisdom that chlorine dioxide reactions with lignin are fast and in the D₀ stage, 90% delignification of the pulp is completed within 10 minutes of contact between the chlorine dioxide and the pulp.

[0009] The industrial experience with conversion of the old C or C_d stage to a D₀ stage, however, has shown a significant decrease in the delignification efficiency as measured by higher chlorine/extraction (CE) or chlorine/extraction with oxygen (E_o) and/or peroxide (CEop) Kappa at a similar or higher active chlorine charge or kappa factor (% active chlorine/kappa) and increased bleaching cost by as much as 20% over elemental chlorine bleaching. Because of much lower reactivity of chlorine dioxide than elemental chlorine toward lignin (particularly nonphenolic lignin) and other impurities, the available retention time and consistency with the old chlorination (C) tower, when used with a chlorine dioxide stage is suboptimal for the D₀ stage operation.

[0010] Further, in the D₀ stage, it has been noted that only about 10-30% of the hexenuronic acid (Hex-A) in the pulp is removed under the operating conditions called for in the D₀ stage of the current elemental chlorine free (ECF) bleach plant. The lower Hex-A removal efficiency in the current D₀ stage is a result of both lower chlorine dioxide reaction efficiency and the absence of the required temperature and retention time for the acid hydrolysis of Hex-A. Hex-A content is an issue particularly for those hardwood species such as eucalyptus, maple, and birch. Hex-A also plays key roles in pulp bleaching chemical consumption, AOX and COD formation, oxalate related scale, and pulp brightness stability. It is known that the use of an acid removal (A) of Hex-A

does not remove lignin, hence an A stage does not contribute to delignification of the pulp.

[0011] As noted, existing bleach plants are not readily convertible to new or different processing conditions which alter the throughput of the pulp being processed and/or affect the follow-on bleaching stages. Such alterations are particularly troublesome if they require costly modification of the existing processing equipment. As a result retrofitting of an existing bleach plant to accommodate different or modified stages of handling of the pulp from the digester through the bleaching operation have heretofore not been feasible from either an operational or an economic standpoint. For example, installation of a new stage in a bleach plant can cost more than \$3 million for an existing ECF bleach plant and therefore is particularly challenging to a capital-limited mature paper industry. In similar manner, deleting a stage from an existing bleach plant for practicing new technology can be a particularly “hard-sell” to a bleaching mill in that the number of stages (and their operating parameters) are well established and proven to produce a pulp having certain characteristics, such as brightness, etc. and any change to this established process normally requires strong reason to make such change.

BRIEF SUMMARY OF THE INVENTION

[0012] In the course of efforts to develop more efficient ECF bleaching technology for cost reduction, the present inventor unexpectedly discovered that if the consistency of the pulp leaving the washer (following the digester) is adjusted to a medium consistency and the time of residence of the pulp in a follow-on delignification stage preceding bleaching stages is extended (D_{emc}) (herein at times referred to as the “extended medium consistency” or “ D_{emc} ” technology), there occurs an unexpected improvement in the delignification efficiency and selectivity, and a lowering of the chlorine dioxide consumption in the overall post-digestion delignification and bleaching process, a reduction of the filtrate volume, a reduction of COD (chemical oxygen demand) and AOX (absorbable organic halides) emissions from the ECF bleaching, decreased oxalate-related scale in ECF bleach plants, improved pulp properties, and an increase in Hex-A removal efficiency over the current short

retention low consistency (LC) D_0 or D_{LC} stage. Moreover, the inventor has found that the D_{emc} technology may be implemented in, and its benefits realized with, existing bleach plants with a minimum of cost and change to the existing bleach plants. The present invention may be employed with pulp which has only been washed after leaving the digester or with pulp which has passed through an O_2 treatment between the digester and the D_{EMC} stage.

[0013] Cutting a bleach plant stage for practicing the D_{emc} technology can be a particularly "hard-sell" to those mills with four-stage bleach plants such as DEopDD or DEopDP. Accordingly, among other things, the present invention provides for existing bleach plants to practice D_{emc} delignification technology for the benefits, in some instances eliminating a bleaching stage or in other instances without cutting the number of bleach stages, all at minimum capital expenditure.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0014] Figure 1 is a schematic flow diagram of a typical prior art digester/bleaching operation as employed in papermaking;

Figure 2 is a schematic diagram including flow patterns of a prior art five-stage bleaching plant;

Figure 3 is a schematic diagram including flow patterns of a first optional retrofit of the five-stage bleaching plant depicted in Figure 2;

Figure 4 is a schematic diagram including flow patterns of a second optional retrofit of the five-stage bleaching plant depicted in Figure 2;

Figure 5 is a schematic diagram including flow patterns of a third optional retrofit of the five-stage bleaching plant depicted in Figure 2;

Figure 6 is a schematic diagram including flow patterns of a fourth optional retrofit of the five-stage bleaching plant depicted in Figure 6.

Figure 7 is a schematic diagram including flow patterns of a prior art four-stage bleaching plant;

Figure 8 is a schematic diagram including flow patterns of a first optional retrofit of the four-stage bleaching plant depicted in Figure 7;

5 Figure 9 is a schematic diagram including flow patterns of a second optional retrofit of the four-stage bleaching plant depicted in Figure 7;

Figure 10 is a schematic diagram including flow patterns of a third optional retrofit of the four-stage bleaching plant with a decommissioned Ep stage (tower and washer) depicted in Figure 7.

10 Figure 11 is a schematic diagram including flow patterns of a fourth optional retrofit of the four-stage bleaching plant depicted in Figure 7.

Figure 12 is a schematic diagram including flow patterns of a prior art three-stage bleaching plant.

15 Figure 13 is a schematic diagram including flow patterns of one embodiment of a retrofit of the three-stage bleaching plant depicted in Figure 12;

Figure 14 is a schematic diagram including flow patterns of a second embodiment of a retrofit of the three-stage bleaching plant depicted in Figure 12; and

20 Figure 15 is a schematic diagram including flow patterns of a third optional retrofit of the three-stage bleaching plant with a decommissioned P stage (tower and washer) depicted in Figure 12.

DETAILED DESCRIPTION OF THE INVENTION

[0015] Retention time and medium consistency are the two synergistic drivers for the present D_{emc} technology and its enhanced delignification performance and other benefits. At the outset, it is noted that neither “medium consistency” nor
25 “extended retention time”, when employed separately (i.e., not in combination) is effective in obtaining the benefits of the present combination which comprises the D_{emc}

technology. "Medium consistency" for present purposes is defined as a consistency of the pulp of at least 10%, and preferably between about 12% and about 15%, based on the weight of oven-dried pulp. "Extended retention time" for present purposes refers to the time which the pulp resides within the D_{emc} stage and may range between about 60 and about 180 minutes. The retention time in the current invention is longer than commercial medium consistency D_0 stage retention time. Lesser retention times reduce delignification efficiency in the present invention and longer retention times do not enhance the desired results.

[0016] Delignification efficiency in a process for conversion of cellulosic material into pulp useful in papermaking is measured by the kappa or K/P number reduction across D_0E_{op} stages while selectivity is manifested by viscosity loss/kappa reduction or filtrate COD/kappa reduction. In the prior art, the D_0 stage comprises delignification employing treatment of a pulp with chlorine dioxide at low consistency and short retention time. The key operations and/or operational parameters of a typical prior art D_0 stage are set forth in Table I above. In D_{emc} delignification according to the present invention, aside from physical and mechanical changes, there is relatively little, if any, change in the operational parameters of the prior art D_0 stage other than pulp consistency and retention time and quantity of chlorine dioxide consumed. Specifically, in accordance with the present invention, the pH and temperature employed in the D_{emc} stage of are unchanged from current prior art operation. In the D_{emc} technology, the D_{emc} stage temperature is determined by that of the incoming pulp from a preceding operation (last brown stock or post- O_2 washer) and there is no steam addition needed. Ideally, the D_{emc} stage would be expected to operate at lower temperature than the current D_0 stage because of the faster chlorine dioxide reaction with lignin at the medium consistency of the present invention than that at low consistency D_0 . To the contrary, the present inventor has found that higher D_{emc} temperature (e.g., 67°C) does not adversely affect D_{emc} delignification performance, in that the chlorine dioxide residual from the D_0 stage has been found to not be as critical as it is for the D1 or D2 bleaching stages.

[0017] On the other hand, the major and important change in converting the delignification stage, D_0 , to a D_{emc} stage lies in the change of the consistency of the

pulp being treated in this stage from a low consistency, i.e., 3-4%, to 10-15% consistency and increase in the retention time of the pulp within the D_{emc} stage from between about 25 and <60 minutes to between 60 and about 180 minutes. As noted, the benefits derived from this combination of medium consistency pulp and extended retention time of the pulp within the stage at the medium consistency are not obtainable by either of these operational parameters taken alone. There is a requirement that both the medium consistency and the extended retention time be employed simultaneously to obtain the benefits found to be provided by the present invention. Table II below shows certain of the benefits obtained by the present invention with respect to the chlorine dioxide usage, the E_{op} pulp P# and the Hex-A removal percentage when processing O₂ hardwood (HW) pulp having an initial kappa of 10.5; a brightness of 45.8%; and a viscosity of 35.6cPs.

TABLE II

Tabl II – Effect of D _o Stage Consistency & Retention Time on D _o E _{op} Performance							
Do Stage Designation	DOLC	DEMC					
Do Retention Time, min	25	75			130		
Do Consistency, %	4	12					
Do CLO ₂ , %	1	0.6	0.8	0.9	0.6	0.8	0.9
Eop pulp brightness, %	69	65.5	68.4	71.2	64.8	69.4	69.7
Eop pulp P#	5.1	4.6	3.3	2.8	4	3.1	2.7
Hex-A Removal, %	20	33	40	54	32	52	58
C mbined Filtrate COD, kg/t	34.99	28.53	27.98	29.98	32.33	31.57	31.09

15 **[0018]** It is noted that, on the average, the chlorine dioxide usage employed in the D_{emc} stage is about 20% less than the prior art D_o stage This is contrary to the expectation of the prior art wherein it is generally understood and practiced that

chlorine dioxide reacts with phenolic lignin within the first ten minutes that the chlorine dioxide is in contact with the pulp, thereby leading one skilled in the art away from the use of extended retention time for less chlorine dioxide in an effort to reduce the kappa or P# of the pulp, and especially away from the present invention wherein not only is there less chlorine dioxide employed, but there also is a reduction in the kappa or P# of the pulp. Additionally, the present inventor has found that the benefits afforded by the D_{emc} technology are not a function of the type (e.g., hardwood or softwood) pulp nor a function of the starting kappa number or lignin content of the unbleached pulp.

[0019] P#, also known as permanganate number is a similar test to kappa, indirectly measuring the lignin content of pulp. Many mills use K number which is similar to P number. Generally, 1 P# or K# is about 1.45-1.5 time kappa #.

[0020] Still further, it is noted that medium consistency, coupled with the extended retention time in the D_{EMC} stage, enhances the removal of Hex-A from the pulp. On the average, the present invention removes 2 to - 5 times as much Hex-A as does the prior art D_o process. In fact, a study on maple hardwood shows that the D_{emc} stage is capable of 70-80% Hex-A removal at a typical chlorine dioxide charge for the current D_{emc} stage, compared with 60% for the prior art hot acid (A) stage employed for Hex-A removal.

[0021] Selectivity can be loosely defined as the ratio of attack on lignin to attack on carbohydrate. Practically, it measures the degree of delignification (kappa reduction) over pulp viscosity or pulp yield loss substituted sometime by filtrate COD – delta kappa/delta viscosity or delta kappa/delta yield or delta kappa / filtrate COD.

[0022] The present D_{emc} technology has been employed in the processing of different varieties of pulp. In addition to the results shown in Table II these tests are set forth in Tables III through VII below and have consistently borne out the benefits of the D_{emc} technology over the prior art D_o technology.

TABLE III

Table III – Effect Of Do Stage Consistency & Retention Time on DoEOP Performance		
Key Do Condition Difference		
Do Stage Designation	DOLC	DEMC
Do Consistency, %	3.5	11
Do retention time, min	45	120
Pulp Properties		
Do brightness, %	43.7	43.7
EOP brightness, %	60.6	59.4
DEK #	5.3	3
DoEOP filtrate COD, kg/t	38.89	32.75
Unbleached Hardwood Pulp: 24.4% brightness, 38.3 cPs viscosity, 15.3 kappa Other bleaching conditions: 1.3% ClO ₂ in Do and 0.2% H ₂ O ₂ in EOP in both cases The DEMC stage uses 0.5% less H ₂ SO ₄ (0.5% vs. 1%) and 0.2% less NaOH (1.2% vs. 1.4%) than DOLC		

[0023] As seen in Table III the same results as set forth in Table II were obtained for a second hardwood pulp. That is, the DEMC stage decreases the DEK number from 3 to 5.3. Surprisingly, the greater delignification efficiency in the DEMC stage is accompanied by reduced filtrate COD, indicating that the DEMC stage results in less non-lignin pulp organic dissolution. This lower COD of less pulp organic dissolution can be translated to less pulp yield loss during ECF bleaching and reduced energy (aeration) expenditure in the waste water treatment plant (WWTP). Generally a 10 kg/t COD can be approximated to a 1% pulp yield loss.

[0024] In the test results reported in Table III, the DEMC stage used 0.5% less H₂SO₄ (0.5% versus 1%) and 0.2% less NaOH in the subsequent EOP stage (1.2% versus 1.4%) than the prior art D^o stage.

[0025] Conventional wisdom teaches that the chlorine dioxide bleaching (D₁ and D₂) stages should be conducted at higher (medium) consistency and longer (120-180

min) retention time to maximize brightness development and shives bleaching. Tests on hardwood and softwood pulps by the present inventor failed to show such difference in pulp brightness, dirt count, viscosity, and filtrate COD between the a D_{1LC} stage and a D_{1MC} stage. In fact slight improvements were shown for the D_{1LC} bleaching than D_{1MC} bleaching in pulp viscosity and filtrate COD, indicating the slightly better bleaching selectivity of the low consistency bleaching than the medium consistency bleaching.

[0026] The temperature in the low consistency D₁ bleaching stage was increased in some cases to compensate for the slower chlorine dioxide reaction rate at low consistency pulp than at medium consistency pulp. As an accompaniment to the present D_{emc} technology, the actual temperature in the low consistency D₁ stage should be practically determined to make sure that all but a trace amount of chlorine dioxide is consumed for good brightness development and shives removal. In general, 170° F is needed for the low consistency D₁ stage to ensure all chlorine dioxide is consumed within the available retention time for brightness and dirt bleaching.

[0027] While all D₁ bleaching tests were conducted at 5% consistency, the D₁ stage at lower consistency (e.g., 4%) is not noted to affect the bleaching results. The consistency of the pulp in the bleaching stages should be maintained at the highest possible, subject to the constraint of the available equipment to minimize the filtrate recirculation and steam demand. These results are shown in Tables IV - VIII below.

TABLE IV

Table IV – Effect Of Consistency and Retention Time on ClO₂ Bleaching Efficiency		
Key D₁ Stage Condition Difference		
D ₁ Stage Designation	D _{1LC}	D _{1MC}
D ₁ Consistency %	5	10
D ₁ Retention time, min	60	120
Pulp Properties		
D ₁ Brightness %	83.4	84.2
D ₁ Viscosity, cPs	26.1	26.6
D ₁ dirt, ppm	0	0
Filtrate COD, mg/l	315	642
Eop Hardwood Pulp: 64.7% brightness, 29 cPs viscosity, 2.2 P# D1 Stage ClO₂ charge: 0.5%		

TABLE V

Table V – Effect Of Consistency and Retention Time on ClO₂ Bleaching Efficiency		
Key D₁ Stage Condition Difference		
D ₁ Stage Designation	D _{1LC}	D _{1MC}
D ₁ Consistency %	5	10
D ₁ Retention time, min	60	120
Pulp Properties		
D ₁ Brightness %	81.5	81.3
D ₁ Viscosity, cPs	23	21.2
D ₁ dirt, ppm	0.04	0.1
Filtrate COD, mg/l	335	684
Eop Hardwood Pulp: 60.8% brightness, 24.1 cPs viscosity, 4.3 P#		

Other D₁ conditions: 0.5% ClO₂ and 0.1% NaOH

TABLE VI

Table VI – Effect Of Consistency and Retention Time on ClO₂ Bleaching Efficiency		
Key D₁ Stage Condition Difference		
D ₁ Stage Designation	D _{1LC}	D _{1MC}
D ₁ Consistency %	5	10
D ₁ Retention time, min	60	120
Pulp Properties		
D ₁ Brightness %	84.8	85.4
D ₁ Viscosity, cPs	21.4	19.9
D ₁ dirt, ppm	0	0.08
Filtrate COD, mg/l	227	598
Eop Hardwood Pulp: 60.8% brightness, 24.1 cPs viscosity, 4.3 P# Other D₁ conditions: 1.5% ClO ₂ and 0.4% NaOH		

TABLE VII

Table VII – Effect Of Consistency and Retention Time on ClO₂ Bleaching Efficiency		
Key D₁ Stage Condition Difference		
D ₁ Stage Designation	D _{1LC}	D _{1MC}
D ₁ Consistency %	5	10
D ₁ Retention time, min	60	120
Pulp Properties		
D ₁ Brightness %	84.3	85.3
D ₁ Viscosity, cPs	24.8	24.6
D ₁ dirt, ppm	0	0
Filtrate COD, mg/l	175	365

Eop Hardw d Pulp: 70% brightness, 26 cPs viscosity, 2.6 P#
Other D₁ c nditi ns: 0.5% ClO₂ and 0.1% NaOH

TABLE VIII

Table VIII – Effect Of Consistency and Retention Time on ClO₂ Bleaching Efficiency		
Key D₁ Stage Condition Difference		
D ₁ Stage Designation	D _{1LC}	D _{1MC}
D ₁ Consistency %	5	10
D ₁ Retention time, min	60	120
Pulp Properties		
D ₁ Brightness %	78.8	78.5
D ₁ Viscosity, cPs	-	-
D ₁ dirt, ppm	0	0
Filtrate COD, mg/l	292	650
Eop Hardwood Pulp: 52.3% brightness, 27.7 cPs viscosity, 3.7 P# Other D₁ conditions: 0.95% ClO ₂ and 0.1% NaOH		

[0028] The advantages of the present invention have been found adequate to justify retrofitting of existing bleach plants to permit use of the D_{emc} delignification technology without cutting short of the current bleach stages.

[0029] It is shown that a short retention time - low consistency chlorine dioxide bleach (D_{1LC}) stage achieves the same or better pulp brightness, dirt count, viscosity, and filtrate COD as those from the currently practiced long retention time - medium consistency bleaching (D_{1MC}) stage. Thus, the current inventor has found that one can use the currently used D₀ tower for bleaching in lieu of the current D₁ or D₂ tower. This factor has been found to permit the practice the D_{emc} technology of the present invention with the existing ECF bleach plant equipment by merely swapping (through piping change) the current D₀ and D₁ tower and their respective functions (delignification and bleaching/dirt removal). In this example, the temperature in the

low consistency (D_{1LC}) bleaching stage (conducted in the formerly D_0 tower) needs to be adjusted based on the available retention time (available for the prior existing D_0 tower) to ensure all of the chlorine dioxide is consumed for brightness and dirt bleaching.

5 **[0030]** The present invention is applicable to all ECF bleach plants (e.g., DEopD, DEopDD, DEopDP, DEopDEpD). As noted the key to improved delignification efficiency and selectivity are medium consistency of the pulp and extended retention time during its first stage treatment (delignification) in the bleaching sequence. Basically, the “old” D_0 stage is made the D_{emc} stage or the D_{emc} technology is implemented in a tower
10 which previously had been employed for a D_1 or a D_2 stage. In either a five, four or three stage bleaching plant, either the D_1 or the D_2 tower currently existing in a bleach plant may be used as the D_{emc} tower (i.e., the first stage) and the currently existing D_0 tower may be used for low consistency (D_{1LC}), a function currently achieved in the D_1 or D_2 stage. As needed, a pretube can be added in front of the D_{1LC} tower to provide
15 extra retention time for balancing the throughflow of pulp through the bleach plant. Thus, in a four or three stage bleaching plant, there is no loss of a stage, hence there is assurance that the ultimately bleached pulp will be equivalent to the bleached pulp produced by the plant prior to the implementation of the D_{emc} technology.

[0031] In accordance with one aspect of the present invention, the inventors
20 have found at least three ways to achieve medium consistency for the D_{emc} operation when retrofitting in an existing ECF mill. First, the current brown or post- O_2 high density (HD) tower low consistency pulp delivery system may be modified as by piping changes, for example, or second, a spare washer may be inserted ahead of the bleach plant as a prewasher, or third, the current last post- O_2 washer after the HD tower
25 pulp delivery system may be switched to a bleach plant prewasher.

[0032] In addition to achieving medium consistency of the pulp, a prewasher achieves additional washing which contributes to reduction of filtrate COD and the overall bleaching cost.

[0033] Figure 1 depicts a typical flow chart for a prior art bleaching plant. As
30 seen in Figure 1, wood chips are loaded into a digester 10, along with a pulping liquor

(white liquor). The digester may be operated on a batch basis or a continuous basis. Continuous digesters are predominant in the present pulp and paper industry. In the depicted embodiment, the output (brown stock) from the digester is fed to a washer 12 wherein the brown stock is washed and further delignified by oxygen (O₂). Spent
5 pulping liquor from the washer may be recycled to chemical recovery. The washed pulp stream from the O₂ washer is fed to a bleach plant 16 wherein the pulp is subjected to a plurality of treatment stages, each designed to convert the pulp to a useable source of papermaking fibers. A typical bleach plant embodying the present invention is adapted to provide an initial delignification stage within the bleach plant,
10 such delignification stage being followed by one, usually two, or more bleaching stages wherein the pulp is treated to develop one or more desired properties of the pulp, depending in a major part on the type of paper to be made from the pulp.

[0034] As noted, the present invention is applicable to all ECF bleach plants (e.g., DEopD, DEopDD, DEopDP, DEopDEpD). Moreover, the present invention is
15 applicable to both softwood and hardwood pulps.

[0035] As noted, the inventor's basic concept for retrofitting currently existing bleaching plants to the use of the D_{emc} technology is to convert one of the bleaching towers (D₁ or D₂, preferably) to the D_{emc} stage. Specifically, the inventor has found that the introduction of the D_{emc} technology into a certain currently existing bleaching
20 plants provides benefits of a nature and degree which permits a given bleaching operation to produce equal or improved bleached pulp while employing one less bleaching stage. This concept precludes the need for additional major equipment expenditure, precludes disruption of the overall balance of flows within the bleaching plant, and requires relatively little expenditure for modifications of the existing
25 mechanical equipment. Primarily the changes involve rerouting piping and as needed the addition of a pretube or the like to provide additional retention time. Should spare or unused equipment, such as a washer, be available in a given plant, this washer may be included in the modified system as desired, again without material capital or modification costs.

[0036] Alternatively, retrofit for the use of D_{emc} technology in the existing ECF bleach plants can be done by converting the current low consistency D_o stage to the D_{emc} stage or by swapping the function of the current D_o and D_1/D_2 stages in which the current D_1/D_2 stage will be used for the D_{emc} stage and the current D_o stage for the D_1/D_2 stage without cutting short of the bleach stages.

[0037] Figure 2 schematically depicts a simplified version of a prior art five-stage bleaching plant wherein digested and washed pulp is fed into a D_o stage, thence through E_{op} , D_1 , E_p , and D_2 stages, thence to a high density (HD) storage tower.

[0038] Figure 3 schematically depicts a first embodiment of a modification to the bleaching plant depicted in Figure 2 wherein the current D_o stage is converted to the D_{emc} stage with the remaining bleaching plant unchanged.

[0039] Figure 4 depicts a second embodiment of a modification to the bleaching plant depicted in Figure 2 wherein the functions of the current D_o and D_1 stages are swapped. The D_1 stage is converted to a D_{emc} stage, and the D_o stage is left in place, but converted to a D_{1LC} stage. In this embodiment, the pulp initially enters the D_{emc} stage, flows through the E_{op} stage, through the D_{1LC} stage, through the E_p stage, through the D_2 stage and is stored.

[0040] Figure 5 depicts a third embodiment of a modification to the bleaching plant depicted in Figure 2 within the D_o stage is eliminated, the E_p stage is converted to a P stage, the D_2 stage is converted to a D_{EMC} stage, and the output from the D_{EMC} stage is piped to the E_{OP} stage. Basically this conversion involves little more than piping modifications.

[0041] Figure 6 depicts a fourth embodiment of a modification to the bleaching plant depicted in Figure 2 within both D_o and E_p stages are eliminated, the D_2 stage is converted to a D_{EMC} stage, and the output from the D_{EMC} stage is piped to the E_{OP} stage. Basically this conversion involves little more than piping modifications.

[0042] Figure 7 schematically depicts a simplified version of a prior art four-stage bleaching plant wherein digested and washed pulp is fed into a D_o stage, thence through E_{op} , D_1 , and D_2 stages, thence to HD storage.

[0043] Figure 8 schematically depicts a first embodiment of a modification to the bleaching plant depicted in Figure 7 wherein the current D₀ stage is converted to the Demc stage with the remaining bleaching plant unchanged.

[0044] Figure 9 depicts a second embodiment of a modification to the bleaching plant depicted in Figure 7 within the functions of the current D₀ and D₁ stages are swapped. The D₁ stage is converted to a D_{emc} stage, and the D₀ stage is left in place, but converted to a D_{1LC} stage. In this embodiment, the pulp initially enters the D_{emc} stage, flows through the E_{op} stage, through the D_{1LC} stage, through the D₂ stage and is stored.

[0045] Figure 10 schematically depicts a third embodiment of a modification to the bleaching plant depicted in Figure 7 wherein the D₀ stage is eliminated, the D₂ stage is converted to a D_{EMC} stage, and the output from the D_{EMC} stage is piped to the E_{OP} stage, thence it flows through the D₁ stage, to restored old Ep (converted to P) stage before to the HD storage..

[0046] Figure 11 schematically depicts a fourth embodiment of a modification to the bleaching plant depicted in Figure 7 wherein the D₀ stage is eliminated, the D₂ stage is converted to a D_{EMC} stage, and the output from the D_{EMC} stage is piped to the E_{OP} stage, thence it flows through the D₁ stage, to the HD storage..

[0047] Figure 12 schematically depicts a simplified version of a prior art three-stage bleaching plant wherein digested and washed pulp is fed into a D₀ stage, thence through E_{OP}, and D₁ stages, thence to the HD storage.

[0048] Figure 13 schematically depicts a first embodiment of a modification to the bleaching plant depicted in Figure 12 wherein the current D₀ stage is converted to the Demc stage with the remaining bleaching plant unchanged.

[0049] Figure 14 depicts a second embodiment of a modification to the bleaching plant depicted in Figure 12 within the functions of the current D₀ and D₁ stages are swapped. The D₁ stage is converted to a D_{emc} stage, and the D₀ stage is left in place, but converted to a D_{1LC} stage. In this embodiment, the pulp initially enters the D_{emc} stage, flows through the E_{op} stage, through the D_{1LC} stage and is stored.

[0050] Figure 15 depicts a third embodiment of a modification to the bleaching plant depicted in Figure 12 within the functions of the current D_0 and D_1 stages are swapped. The D_1 stage is converted to a D_{emc} stage, and the D_0 stage is left in place, but converted to a D_{1LC} stage. The old decommissioned E_p tower is converted to the P stage.

[0051] Table IX lists various permissible retrofits of current bleaching sequences.

TABLE IX

Current Sequence	P tential DEMC Sequence	P tential Bl aching Operati ns
DE _{OP} DE _P D	WD _{EMC} E _{OP} DP	Current D ₂ Washer as prewasher (W) Current D ₂ tower for DEMC Current D ₀ washer for DEMC washer Current E _P to P stage Spare current D ₀ tower
	DE _{MC} E _{OP} DE _P D	Current D ₀ to DEMC stage
	DE _{MC} E _{OP} D _{LC} E _P D	Swap the current D ₀ and D ₁ stages
	WD _{EMC} E _{OP} D	1 st case plus spare current E _P tower and washer
DE _{OP} DD	WD _{EMC} E _{OP} D	Current D ₂ washer as prewasher (W) Current D ₂ tower for DEMC Current D ₀ washer for DEMC washer Spare current D ₀ tower
	DE _{MC} E _{OP} DD	Current D ₀ to DEMC stage
	WD _{EMC} E _{OP} DP (for the mills with spare old E _P stage)	Current D ₂ washer as prewasher (W) Current D ₂ tower for DEMC Current D ₀ washer for DEMC washer Spare E _P (if the mill has) to P stage Spare current D ₀ tower
	DE _{MC} E _{OP} D _{LC} D	Swap the current D ₀ and D ₁ stages
DE _{OP} D	DE _{MC} E _{OP} D	Current D ₀ to DEMC stage
	DE _{MC} E _{OP} D _{LC}	Swap the current D ₀ and D ₁ stages
	DE _{MC} E _{OP} D _{LC} P	Swap the current D ₀ and D ₁ stages Spare E _P (if the mill has) to P stage

		Spare E _P (if the mill has) to P stage
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[0052] Table X shows the results of the stage-by-stage bleaching performance, the current bleaching as a benchmark in the left column of Table X and D_{EMC} sequence on the right. In this simulated modification of a typical four stage bleach plant employing a D₀E_{OP}D₁D₂ bleaching sequence, the D₀ stage was converted to a

5 D_{EMC} stage with all other stages remaining the same. Two additional simulated modifications of the prior art D₀E_{OP}D₁D₂ bleach sequence were performed for WD_{EMC}E_{OP}D₁LC_{D2} and WD_{EMC}E_{OP}DP sequences, where “W” represents a spare washer present within the plant. The results are summarized in Table X. As expected, placing

10 a prewasher stage before the D_{EMC} delignification stage improves overall brightness development in each of the two conversions. In the second of these two modifications, a significant improvement in final pulp brightness stability was achieved due to placing the P stage at the end of the sequence. Additional benefits of these two modification were higher pulp viscosity and lower filtrate emissions in the form of COD.

TABLE X

Table X - Bleaching Performance Summary					
Retrofit Case	Control		Case 1	Case 2	Case 3
Bleach Sequence	D₀LC_{EOP}DD	D₀LC_{EOP}DD	D_{EMC}E_{OP}D_{LC}D	W_{DEMCEOP}D_{LC}D	W_{DEMCEOP}DP
ClO ₂ , %	2.95	2.95	2.05	2.05	1.85
H ₂ O ₂ , %	0.2	0.2	0.5	0.5	0.7
NaOH, %	1.8	1.8	1.4	1.3	1.65
H ₂ SO ₄ , %	1	1	0.5	0.5	0.5
MgSO ₄ , %	0	0	0.1	0.1	0.1
Pulp & Filtrate Properties					
Brightness, %	87.1	87.3	86.7	87.7	87.5
Rev Brightness, %	85	85.1	84.5	85.6	86
Viscosity, cPs	20.6	20.9	23.5	24.4	22.6
Tappi Dirt, ppm	0	0	0	0	0
COD, kg/t	43.87	43.8	37.64	39.02	42.69
Net Benefits					
Cost Reduct., \$/t	Control	Control	6.18	6.31	6.13
COD Reduct., kg/t	Control	Control	6.23	4.78	0.11
Bleach Yield, %	Control	Control	0.6	0.45	0
Cost Basis: ClO ₂ -\$0.35/#, H ₂ O ₂ -\$0.2/#, NaOH-\$0.13/#, H ₂ SO ₄ -\$0.04/#, MgSO ₄ -\$0.18/#					

[0053] The retrofit costs for the D_{EMC} delignification as shown in Case 1

(D_{EMCEOPDLC}D) of Table X are, 1) Modifications of current brown HD pulp delivery from

5 low consistency to medium consistency ready for the D_{EMC} stage operation and the

2) The repiping relating to swapping the D₀ with the D₁ stage.

[0054] Upgrading the current spare E₂ washer for a bleach plant prewasher is part of the retrofit strategy in both Cases 2 and 3. Repiping was needed to reconfigure the bleach plant to include the added changes.

[0055] The retrofitting strategy for Case 2 (W_{DEMCEOPD_{LC}D}) includes upgrading the spare E₂ washer for a bleach plant prewasher to obtain medium consistency for the D_{EMC} stage operation in addition to bleach stage repiping to accomplish the exchanging of the functions of the current D₀ and D₁ stages.

[0056] Similarly, Case 3 (W_{DEMCEOPDP}) requires upgrading the current spare E₂ washer for a bleach plant prewasher and the E₂ tower for the P stage. Either a current D₁ or D₂ stage can be used for the new D_{EMC} stage operation.

[0057] As the results in Table X show, the improved delignification efficiency using the D_{EMC} technology contributed to a significant amount of chlorine dioxide savings (19 lb/ton) along with reductions in NaOH and H₂SO₄ usage relating to the increased D₀ stage consistency. The peroxide usage in the D_{EMC} technology is adjusted to be consistent with the general industry trend in H₂O₂ usage in ECF bleaching. An average peroxide usage in the E_{OP} stage of the modern ECF bleach plants is 0.7-0.8%. The ECF bleach plants with O₂ delignification operation usually use less peroxide in the E_{OP} stage because of less brightness development at higher H₂O₂ usage due to pulp's pre-exposure to similar chemistry in the O₂ stage.

[0058] Suboptimal peroxide usage in a current ECF bleach plant is due to the desire to maximize pulp viscosity preservation. A 2 lb/ton M_gSO₄ addition was therefore accompanied with increased peroxide use in the D_{EMC} ECF bleaching sequence. The net results of a 6 lb H₂O₂ increase and 2 lb M_gSO₄ addition are 8% points (from 60% to 68%) higher E_{OP} pulp brightness and almost 3 points higher bleached pulp viscosity, as seen from Table X.

[0059] The filtrate COD is significantly decreased after retrofitting conversion of the prior art four-stage bleach sequence to the D_{EMC} sequence shown in Table X. Since filtrate COD reflects the amount of organic dissolution from pulp during bleaching, the reduced filtrate COD manifests the improved bleaching selectivity of the

D_{EMD} technology over the current four-stage bleaching sequence and represents the reduction in pulp yield loss during the bleaching operation.

[0060] The overall results of the simulated modifications discussed above are consistent with actual mill experience. Notably, the results show about \$6/ton or \$1.5 MM/year bleaching cost reduction, plus enhanced pulp brightness, reverted brightness, pulp dirt count and viscosity attributable to the implementation of the D_{emc} technology. The improved bleaching selectivity is translated to about 5kg/ton COD reduction, representing about 0.5% pulp yield increase and potential decrease in energy in the WWTP. All these results are consistent with the demonstrated improved delignification efficiency and selectivity of the D_{emc} technology over the prior art bleaching sequences from full-scale operations of other mills and lab studies of pulps.

[0061] Mills which use high hexenouronic acid (Hex-A) content hardwood species such as eucalyptus, maple, and birch, suffer from low delignification efficiency (measured traditionally by the pulp kappa difference before and after the O₂ delignification stage). This is due primarily to the inability of O₂ to remove part of the kappa which is attributable to the pulp Hex-A content. For example, a maple pulp has a high Hex-A content and only about 30% delignification is achieved by a conventional oxygen stage.

[0062] High Hex-A content of a pulp not only interferes with the delignification efficiency in the oxygen stage, but also inhibits the delignification efficiency in the first two stages (D_oE_{op}) of a prior art ECF bleaching plant. In one example, the first two stages of a bleach plant may achieve only about 40% delignification efficiency at kappa factor of about 0.26 in the D_o stage with as much as 13 cPs unit viscosity loss. This is due largely to the inability of the currently employed low consistency, short retention time D_o stage of the prior art to effectively and selectively remove Hex-A.

[0063] Hex-A plays key roles in pulp bleaching chemical consumption, AOX and COD formation, oxalate-related scale, and pulp brightness stability particularly for hardwood species.

[0064] Hex-A reacts with permanganate and therefore contributes to a significant amount of kappa number of unbleached pulps from a digester or after oxygen delignification in a manner similar to lignin. Hex-A is reactive towards electrophilic bleaching chemicals such as chlorine dioxide in the D₀, D₁ or D₂ stages (more precisely Cl₂ and HOCl generated during ClO₂ reactions with lignin) and ozone in the Z stage, but stable toward nucleophilic chemicals such as O₂ in the O₂ stage and H₂O₂ in the E_{OP} and E_P stages. Therefore, Hex-A behaves similarly to lignin of the unbleached pulp and contributes to chlorine dioxide consumption in the D₀ stage. Oxidation of Hex-A increases the concentration of oxalate in filtrate, which can potentially lead to increased scale in bleach plant equipment. Hex-A contains unsaturated groups responsible for bleached pulp brightness reversion, if not removed.

[0065] The Hex-A content in pulp depends on wood species and cooking conditions. Hardwood (HW) pulps contain much higher Hex-A than softwood (SW) pulps due to higher native xylan content in HW than SW species and milder cooking conditions, i.e., lower alkali concentrations, for HW than for SW. SW cooking typically experiences a fast rise in Hex-A during the heating up period followed by a gradual degradation of Hex-A in the subsequent delignification period. In contrast, Hex-A content continues to rise throughout the HW cooking period. The rate of Hex-A degradation increases with increasing OH⁻, HS⁻, and ionic strength of cooking liquor as well as increasing temperature. Higher alkali residual with the modern modified cooking techniques drops the Hex-A content in pulp.

[0066] Eucalyptus, maple and birch are known to contain high Hex-A content among the HW species. For example, the contributions of Hex-A to chlorine dioxide consumption and filtrate properties during ECF bleaching of O₂ delignified eucalyptus kraft pulp, is reported in the literature. The contributions from residual lignin are also listed for reference. This data is given in Table XI.

TABLE XI

Table XI – Characterization of Hex-A contributions of Eucalyptus Pulp						
	Kappa	Total ClO₂ Consumption	OX, g/ton	AOX, g/ton	COD, kg/ton	Oxalate
Hex-A	5.19		55.2	197	7.57	
% Contribution	62	42.4	35.5	37.9	40	35.5
Residual Lignin	3.1		62.7	37.4	8.49	
% Contribution	48	41.61	40.4	12.2	45	30

[0067] Separate studies show that Hex-A in maple species accounts for about 3K# (4.4 kappa) before O₂ delignification and 2.8 - 2.9 K# after O₂ delignification.

5 These results are shown in the following TABLE XII.

TABLE XII

Table XII – Contribution of Hex-A to Pulp K# of Maple				
Pulp Before O₂ Delignification (#2 BSW)				
Pulp Sample	Hex-A ug/g	Initial K#	Final K#	K# from Hex-A
#1	3756.8	9.8	6.9	2.9
#2	3889.0	10.2	6.5	3.7
Pulp After O₂ Delignification (#1 PoW)				
#1	3000.7	7.7	4.9	2.8
#2	3550.4	7.6	4.7	2.9

*Hex-A removed

[0068] Hot acid (A) treatment is considered as an effective means to selectively remove Hex-A (by about 60%) prior to chlorine dioxide delignification, hence reduction of the chlorine dioxide consumption by the Hex-A. Hot acid treatment, however,

10 requires a significant amount of retention time (usually 90-120 minutes), high

temperature (75°-90° C), and an acidic pH (2.5-3.5). These operating parameters require a large acid resistant tower, hence a very large capital expenditure (\$1.5 - \$3 million). Moreover, the large amount of acid required for the reaction and the large amount of steam required to develop and maintain the high temperature add to the overall cost of an A stage.

[0069] The currently used D₀ stage of an ECF bleach plant removes a very limited amount (10%-30%) of the Hex-A in a hardwood pulp. This is at the expense of consumption of the chlorine dioxide. The lower Hex-A removal efficiency in the prior art D₀ stage (low pulp consistency and short retention time) has been noted to be due to both lower efficiency (diffusion, reactions, etc.) and insufficient retention time required for acid hydrolysis.

[0070] In accordance with one aspect of the present invention employing D_{emc} technology in the initial delignification stage, the present inventor discovered that there occurs simultaneous enhanced delignification plus Hex-A removal, hence reduction of the chlorine dioxide demand, as well as environmental (filtrate volume, COD/AOX emission) and operation and quality improvement, all at reduced cost.

[0071] TABLE XIII below illustrates the performance difference between the prior art D₀ technology and the present D_{emc} technology from another mill study.

TABLE XIII

Table XIII - Lab Investigation of O₂ Delignified Pulp				
	Pulp #1		Pulp #2	
Sequence	D_{Lc}E_{OP}	D_{EMc}E_{OP}	D_{Lc}E_{OP}	A_DEMcE_{OP}
E _{OP} Brightness, %	78.7	85.3	73.7	81.9
E _{OP} P#	3.5	1.2	5.1	2
E _{OP} Viscosity	19.2	21.8	19.1	28.4
Filtrate COD, kg/t			50.05	44.6
Where A-is acid treatment with H ₂ SO ₄ Pulp #1- 52.6% brightness, 27.7% cPs viscosity, and 6.3 P#				

Pulp #2- 41.2% brightness, 32.9% cPs viscosity, and 10.8 kappa or 7.4 P#

[0072] Laboratory studies by the present inventor on HW pulps for an operating mill (collected at two different times with different unbleached pulp kappa or P# and brightness) consistently showed that the prior art D_{oLC} stage is not only inefficient (about 33% and 44% P# reduction in the D_{oEOP} stages), but also very non-selective (at the expense of 8.5 and 13.8 viscosity drop in these stages). In comparison, the present D_{emc} stage significantly increases P# reduction efficiency in the first two stages over the prior art D_{oLC} stage to 80-81% while reducing viscosity loss to about 5 cPs. The improved delignification selectivity of the D_{emc} stage is also manifested by 10% reduction in filtrate COD, which can be translated to a higher pulp yield over the prior art D_{oLC} stage. It is noted that P# and previously used K# are similar terms used to indicate the lignin and Hex-A content in the pulp.

[0073] The low P# reduction efficiency of the prior art $D_{oLC}EOP$ stages (shown in Table XIII) is due to the high content of Hex-A in HW pulps (esp. maple) and the relative inability of the prior art to remove the Hex-A. Assuming a delignification efficiency of 70% in the prior art $D_{oLC}EOP$ stages (normally, $D_{oLC}EOP$ stages achieve 70-80% delignification at a kappa factor of 0.2-0.3 in the D_o stage), the $D_{oLC}EOP$ stages remove only about a calculated 13% of the Hex-A in the HW pulp as shown in TABLE XIV below.

TABLE XIV

Table XIV - Lignin and Hex-A Removal Efficiency in the $D_{oLC}EOP$ Stages on Pulp #1			
	Lignin	Hex-A	Total
Unbleached Pulp P#	3.5	2.8	6.3
$D_{oLC}EOP$ Pulp P#	1.05	2.45	3.5
Removal Efficiency, %	70	13	44

[0074] Further, assuming 80% delignification by the $D_{emc}E_{op}$ stages (10% higher than that of the $D_{OLC}E_{OP}$ stages), it is derived that the $D_{emc}E_{op}$ stages simultaneously remove 82% Hex-A from the pulp. This is shown in TABLE XV below.

TABLE XV

Table XV – Lignin and Hex-A Removal Efficiency in the $D_{emc}E_{OP}$ Stages on Pulp #1			
	Lignin	Hex-A	Total
Unbleached Pulp P#	3.5	2.8	6.3
$D_{emc}E_{OP}$ Pulp P#	0.7	0.5	1.2
Removal Efficiency, %	80	82	81

[0075] Since E_{op} is incapable of significantly removing Hex-A from the pulp as is possible in an O_2 stage, it is observed that it is the chlorine dioxide that removes the majority of the Hex-A in the pulp at the conditions present in the D_{emc} stage.

[0076] TABLE XVI below is a performance comparison between $D_{emc}E_{op}$ stages and $AD_{emc}E_{op}$ stages and shows that addition of a hot acid (A) treatment on maple pulp #2 does not achieve additional P# or Hex-A reduction efficiency improvement over the $D_{emc}E_{op}$ stages treating pulp #1, suggesting that the function of the D_{emc} and A stages are overlapping and redundant in terms of their ability to remove Hex-A. In fact, addition of an A stage to the $D_{emc}E_{op}$ stages resulted in an overall lower delignification and Hex-A removal efficiency (by comparing the results of the two pulps in Table XVI) implying potential interference of the A stage with the D_{emc} stage performance. The potential interference of the A stage with the D_{emc} stage delignification efficiency leads to a conclusion on the potential synergistic effect of Hex-A oxidation products, e.g. oxalate, on lignin removal (delignification) efficiency in the D_{emc} stage.

TABLE XVI

Table XVI- Performance Comparison Between DEMcEOP and A DEMcEOP Stages						
	Pulp #1 w/ DEMcEOP			Pulp #2 w/ A DEMcEOP		
	Lignin	Hex-A	Total	Lignin	Hex-A	Total
Unbleached Pulp P#	3.5	2.8	6.3	4.6	2.8	7.4
DEMcEOP Pulp P#	0.7	0.5	1.2	1.38	0.62	2
Removal Efficiency, %	80	82	81	70	78	80

[0077] Further, for mills which are currently processing high Hex-A pulps species (e.g., maple) and currently employing a D_{oLC} stage, it is more cost-effective to invest in D_{emc} technology to enhance both Hex-A and lignin removal efficiency than to invest in the addition of an A stage to achieve Hex-A removal only.

[0078] The advantages of the D_{emc} technology over the prior art D_o (which is carried out with low consistency pulp) technology indicates the importance of higher concentration (as a result of higher pulp consistency) and longer retention time in the removing of Hex-A from the pulp, along with the other noted advantages of the D_{emc} technology. As has been demonstrated by the present inventor, the improved efficiency and selectivity of the D_{emc} technology emanates from (a) increased consistency of the pulp (higher chemical concentrations leading to faster reaction kinetics and mass transfer as well as longer retention time) and (b) extended retention time which benefits only at medium consistency of the pulp.

[0079] Given the complex reactions occurring simultaneously in the initial delignification stage of digested pulp treatment (either D_o or D_{emc} stage) - some being productive and some being unproductive - increased pulp consistency and chemical concentration can alter the ratio of productive to unproductive chemical reactions in this initial stage toward ultimately positively affecting delignification efficiency and selectivity. For example, from a reaction mechanism point of view, high consistency and chemical concentrations favor formation of ClO₂ over ClO₃⁻, minimizing wasting

oxidizing power of ClO_2 . It is also postulated that increasing the concentration and duration of more effective delignification chemicals such as ClO_2 and HOCl in the D_{emc} stage as a result of increased pulp consistency, leads to overall enhanced delignification efficiency. The enhanced efficiency and selectivity may be by increasing the concentration of efficiency-enhancing components (produced in the D_{emc} stage) to a critical level as a result of the increase in pulp consistency that is not possible in the low consistency D_0 stage. One example may be increased oxalic acid or oxalate concentration formed in oxidation of lignin and Hex-A in the D_{emc} stage.

[0080] Again, recognizing the complexity of the chemical reactions which take place in an initial chlorine dioxide-based delignification stage of digested pulp, and whereas the present invention is not intended to be limited to any particular chemical reaction or combination of chemical reactions within an initial chlorine dioxide-based delignification stage. It is believed that medium consistency pulp leads to high chemical concentrations at a given reactor volume and chemical charge and a fast delignification rate. The higher the consistency, the faster the delignification kinetics. High chemical concentration maintains high driving forces and improves overall reaction efficiency and selectivity by minimizing secondary reactions. Like O_3 , the ClO_2 delignification process is generally considered to be diffusion controlled because of the low delignification activated energy (52-64 kJ/mol). High pulp consistency aids the diffusion process by maintaining high ClO_2 concentration and decreasing the thickness of the diffusion layers. Increasing D_0 consistency from the prior art 3 - 3.5% to 10% or higher increases the D_0 stage retention time by 3 times the prior art time, e.g. from 30 min. to 90 min. From a reaction mechanism point of view, high consistency pulp and chemical concentration favors formation of ClO_2 over ClO_3 , minimizing wasting oxidizing power.

[0081] With respect to the effect of retention time of the pulp within the reactor vessel, ClO_2 reacts with lignin (particularly nonphenolic lignin) much slower than elemental chlorine and similar to oxygen, chlorine dioxide delignification is typically represented by two-phase reaction kinetics. The long retention time improves chlorine dioxide delignification and subsequent extraction efficiency by completing

secondary slow delignification reactions with nonphenolic lignin in the chlorine dioxide delignification stage of the pulp.

[0082] In any event, the benefits of both retention time and consistency of the pulp are evident in the D_{emc} stage is shown in the following TABLES XVII , XVIII, and XIX.

TABLE XVII

Table XVII – Synergistic Effect Of Retention Time And Medium Consistency Do Brightness			
Do CLO₂ Charge, %	0.4	0.75	1
4% CSC & 25 min in Do	70.6	72.2	73.6
12% CSC & 25 min in Do	72.1	75.6	76.7
12% CSC & 130 min in Do	72.1	76.4	78.2

TABLE XVIII

Table XVIII – Synergistic Effect Of Retention Time And Medium Consistency On E_{op} Brightness			
Do CLO₂ Charge, %	0.4	0.75	1
4% CSC & 25 min in Do	75.4	75.5	78.7
12% CSC & 25 min in Do	76.8	79.8	82
12% CSC & 130 min in Do	77.9	83.4	85.3

TABLE XIX

Table XIX– Synergistic Effect Of Retention Time And Medium Consistency on E_{op} P#			
Do CLO₂ Charge, %	0.4	0.75	1
4% CSC & 25 min in Do	3.9	3.7	3.5

12% CSC & 25 min in Do	3.4	3	2.7
12% CSC & 130 min in Do	3.4	2.3	1.2

[0083] However, the beneficial effect of retention time in the D_{emc} stage is absent in the prior art D_{oLC} stage as shown in TABLE XX below. In short, there is no effect on retention time in the prior art D_{oLC} stage.

TABLE XX

Table XX – Synergistic Effect Of Retention Time In Low Consistency (3.5%) Do Delignification			
Retention Time, min	30	90	180
Temperature, C	60	58	55
CLO₂, %	1.1	1.1	1.1
Do Brightness, %	51	51	50.2
E_{op} Brightness, %	72	72.4	71.3
E_{op} P#	2.5	2.5	2.4

[0084] The enhanced Hex-A removal and overall P# reduction efficiency in the D_{emc} stage over the prior art D_{oLC} stage could also imply (a) the potential synergistic effects of Hex-A oxidation products, e.g., oxalate, on lignin removal (delignification) efficiency in the D_{emc} stage because of their reaching critical concentrations which is not possible in the prior art D_{oLC} stage and/or (b) the extended acid hydrolysis in the D_{emc} stage which may contribute to the enhanced Hex-A removal that is absent in the prior art D_{oLC} stage. Implication (a) points to the importance of higher consistency and implication (b) points to extended retention time.

[0085] Whereas the present invention has been described at times in specific terms and specific examples, it is intended that the invention be limited only as set forth in the Claims appended hereto.